

Removal of Anionic Metal Ions from Wastewater by Hydroxide-type Adsorbents

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Abstract: Generally speaking, anionic metal concentrations in wastewater from industries and mineral processing plants are well above the allowed limits for effluent set by the Ministry of Environment of Japan. Nowadays, the removal of anionic ions has been considered difficult and development of new process is desperately needed. In this paper, we report the development of three hydroxide-type adsorbents, illustrating their adsorption efficiency in removing As, Se, Mo and Sb ions from aqueous solutions. The main finding of this work was that the adsorption behavior was influenced very much by both the pH and the adsorbent concentration. Nevertheless, the newly developed hydroxide-type adsorbents were very effective in reducing the concentration of those anionic ions.

Key words: hydroxide-type adsorbent; adsorption; anionic metal ions; removal; wastewater

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1 INTRODUCTION

In Japan, the environment regulations have been implemented in accordance with the basic laws for controlling the environmental pollution and conserving the natural resources. These laws have created the legal base for reducing the concentration of heavy metals in the environs. In this frame many effluent standards (ES) have been set for water pollutants to maintain the quality of public water supply. For example, the effluent standard of selenium or arsenic and their compounds is 0.1 mg/L, while those of molybdenum and antimony are 0.07 and 0.02 mg/L respectively.

In aqueous solution, arsenic and selenium exist mainly as anionic ions. These species are toxic elements, and their mobility and concentrations in the environment have important implications for the health of humans, animals and plants^[1]. Arsenic poisoning can range from white or dark spot of the skin, skin hardening and skin cancer. Other forms of cancer such as lung and kidney may also result. Thus, the removal of arsenic ions from wastewaters is an important issue, especially for many abandoned mines in Japan, where the co-precipitation process with ferric/ferrous ions by neutralization is used to remove arsenic ions. Nevertheless, arsenious ion (AsO_3^{3-}) is difficult to co-precipitate, compared with arsenic ion (AsO_4^{3-}).

Selenium, on the other hand, is used for production of semiconductors and pigments. Selenium at low level is essential in the diet of human and many animals, but

at high concentration can be quite toxic. For instance, selenium, accumulated in certain plants in large quantity, is harmful to animals and humans when ingested, preventing proper bone formation. Regarding the chemistry of selenium, it should be noted that the selenite [Se(VI)] shows a strong affinity for iron oxide surfaces^[2-5], while selenate [Se(IV)] is not adsorbed onto oxide surfaces and can easily be transported in ground water^[1,6,7]. For pH and redox conditions that prevail in most aqueous environments, selenium exists as an oxyanion in the forms of selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), or biselenite (HSeO_3^-)^[8]. Molybdenum is generally used as additive in special steel and lubricant (MoS_2). Molybdenum exists as an oxyanion in the form of molybdate (MoO_4^{2-}). Antimony, on the other hand, is mainly used as flame-retardants. Antimony can be emitted to the environment as volatile species (e.g. SbH_3), solutes (e.g. SbO_2^-) and solids (e.g. Sb, Sb_2O_3 or Sb_2O_5) of different valence states^[8,9].

Considerable efforts are being made to determine the factors that influence the adsorption of anions such as arsenic and selenium^[10,11]. In this paper, the authors report the development of hydroxide ion-type adsorbents for the removal of As(III), Se(VI), Mo(VI) and Sb(III) compounds.

2 EXPERIMENTAL

2.1 Synthesis of Hydroxide-type Adsorbent

Three types of hydroxide powders have been

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prepared as adsorbents. These are: (1) ferric hydroxide, which has been precipitated (at 298 K) by adding sodium hydroxide in ferric chloride aqueous solution at about neutral pH^[12]; (2) ferric cupric hydroxide, which has been synthesized (at 298 K) by mixing 2 mol/L ferric nitrate and 1 mol/L cupric nitrate solution and adding sodium hydroxide solution until the neutral pH was reached^[13], and (3) ferric lead hydroxide, which has been synthesized (at 298 K) by mixing 2 mol/L ferric nitrate and 1 mol/L lead nitrate solution and adding sodium hydroxide solution until pH 11 was reached^[14-16]. The synthesized powders are used as adsorbents, after being dried at 333 K for 70 h. X-ray diffraction analysis indicated that these adsorbents were of almost amorphous structure.

2.2 Artificial Wastewater

Dilute arsenite (As_2O_3), sodium selenate (Na_2SeO_4), ammonium molybdate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$] and antimony(III) chloride (SbCl_3) standard solutions are used as artificial wastewater samples. The concentration of each ion [i.e. As(III), Se(VI), Mo(VI) and Sb(III)] in aqueous solutions ranged from 10 to 50 mg/L.

2.3 Adsorption Experiments

Adsorption experiments were conducted by introducing one of the prepared adsorbents into the artificial wastewater containing one of the ions, i.e. As(III), Se(VI), Mo(VI) or Sb(III), and agitating the suspension for 2 h. The temperature was kept constant (i.e. 298 K), while the pH of the solution was controlled by adding weak HCl or NaOH. Finally, after filtrating the suspension, the filtrate was analyzed by ICP.

3 RESULTS AND DISCUSSION

3.1 Removal of Arsenic(III) Ion

The distribution of As(III) species and the total adsorbed As(III), (denoted by "Total ADS As"), as a function of pH is shown in Fig.1, when ferric hydroxide

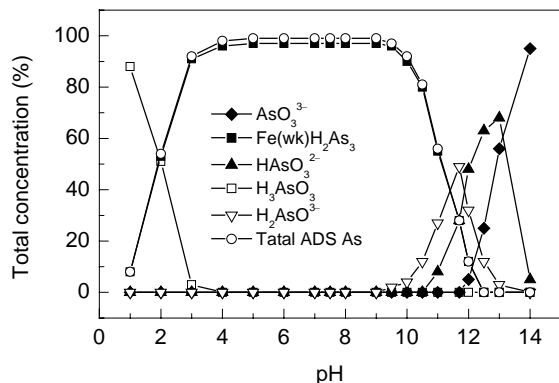


Fig.1 The distribution of As(III) species and the total adsorbed As (Total ADS As) as a function of pH

was used as adsorbent. The diagram has been drawn by using MINEQL+ software for chemical equilibrium modeling system. Fig.1 shows that the As(III) ions change their form as the pH of the system varies. It can also be seen that As(III) is adsorbed onto the surface of the adsorbent (i.e. ferric hydroxide), while pH ranges between 4 and 9 (Fig.1). Fig.1 also shows that at pH lower than 2 the main species in the solution are H_3AsO_3 . On the other hand, at alkaline conditions As(III) exists as H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-} ions.

Moreover, Fig.2 shows the effect of pH on the removal rate of As(III) ion by ferric hydroxide. The initial concentration of arsenic in the sample was 40 mg/L, whereas the initial concentration of ferric hydroxide was 10 g/L. The sample was mixed for 2 h, before being analyzed for arsenic. It can be seen that at acidic conditions the concentration of arsenic is relatively high, nevertheless at pH 6 almost all the arsenic has been removed from the aqueous solution and the adsorbed amount reaches its maximum.

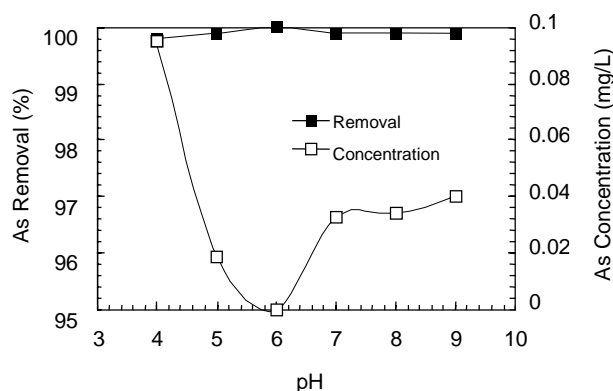


Fig.2 The effect of pH on removal of arsenic (III) ion by adsorbent of ferric hydroxide powder (conditions: adsorption period 2 h; 298 K; initial concentration of As 40 mg/L; adsorbent 10 g/L)

Figure 3 shows the Langmuir isotherm of arsenic in water. This is a quantitative relationship, which describes the equilibrium between the concentration of the adsorbate in solution (in mg/L) and its sorbent concentration (in mg/g). The term isotherm is used to signify that the relationship is for a given temperature^[17]. The linearized form of the isotherm is given by Eq.(1).

$$\frac{1}{q} = \frac{1}{q_m K_{\text{ads}}} \left(\frac{1}{C} \right) + \frac{1}{q_m}, \quad (1)$$

where q is the sorbent concentration, (mass adsorbate/mass adsorbent); q_m is the maximum capacity of the adsorbent for adsorbate (mass adsorbate/mass adsorbent); C is aqueous concentration of adsorbate (mass/volume); K_{ads} is a measure of affinity of adsorbate

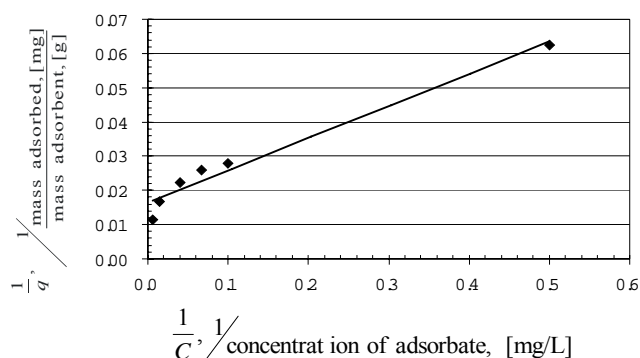


Fig.3 Langmuir isotherm of As(III) (conditions: ferric hydroxide 0.5 g/L; agitation time 2 h; pH 6.5; T 298 K; initial concentrations of As 10, 20, 30, 50, 100 and 200 mg/L) for adsorbent.

In order to collect the data to construct this isotherm, 0.5 g/L ferric hydroxide was added in the water samples containing arsenic (As) at various concentrations, and mixed for 2 h. The pH of solution was 6.5 and the temperature 298 K. The concentration of arsenic remaining was then measured by ICP. By knowing the initial concentration, the sorbed concentration was calculated. The data have then been interpolated using the least-square linear regression in order to calculate the maximum capacity of the adsorbent. It was found that the maximum capacity of ferric hydroxide for arsenic was 61 mg/g. The photograph of the surface of adsorbent (i.e. ferric hydroxide), where $\text{Fe(III)(OH)}_2\text{-H}_2\text{AsO}_3$ would have been formed on the surface of adsorbent, is shown in Fig.4. It should be noted that the adsorbed arsenic can be eluted at pH more than 13 and recovered in the concentrated aqueous phase.

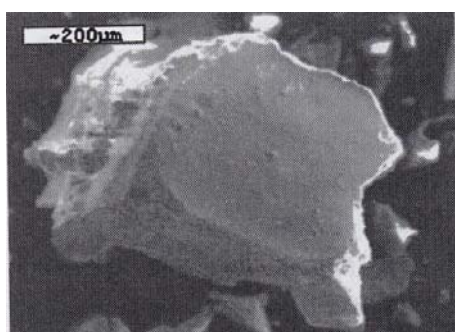


Fig.4 Surface of adsorbent after As(III) adsorption

3.2 Removal of Selenium(VI) Ion

The distribution of Se(VI) species and the total adsorbed Se (denoted by "Total ADS Se") as a function of pH is shown in Fig.5, when ferric cupric hydroxide was used as adsorbent. The diagram has been drawn by using MINEQL+ software for chemical equilibrium modeling system. The diagram shows that the total

concentration of the sorbed Se(VI) reached its peak at pH 3. It also shows that the total concentration of the adsorbed Se(VI) decreases sharply at pH more than 5, where the main aqueous species is SeO_4^{2-} .

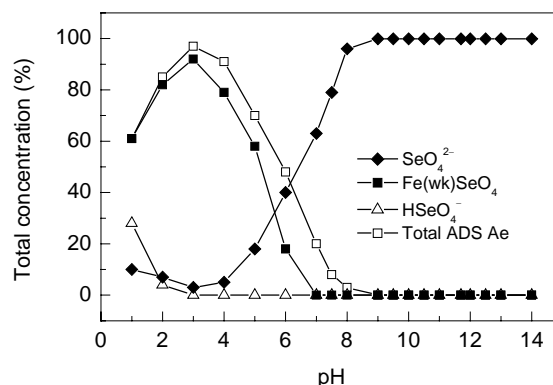


Fig.5 The distribution of Se(VI) species and the total adsorbed As (Total ADS Se) as a function of pH

Figure 6 shows the effect of pH as a function of the adsorption capacity of Se(VI) ion and concentration of copper, when ferric cupric hydroxide is added in the Se(VI)-containing aqueous solution. The selenium adsorption capacity is dependent of the pH of solution and it decreases at higher pH value (Fig.6). Moreover, cupric ions were released into aqueous solution in mainly the acidic region (Fig.6).

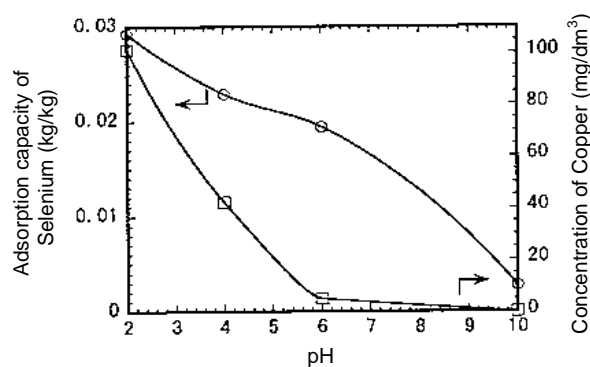


Fig.6 The effect of pH on removal of selenium (VI) ion by adsorbent of ferric cupric hydroxide powder (\circ : adsorption capacity; \square : concentration of copper; conditions: adsorption period 2 h, $T=298$ K)

The Langmuir isotherm of selenium in water is shown in Fig.7. In order to collect the data to construct the isotherm, 1 g/L ferric cupric hydroxide was added in the water samples containing selenium at various concentrations, and mixed for 2 h. The pH of solution was 6 and the temperature 298 K. It was found that the maximum capacity of ferric cupric hydroxide for selenium was 23.6 mg/g.

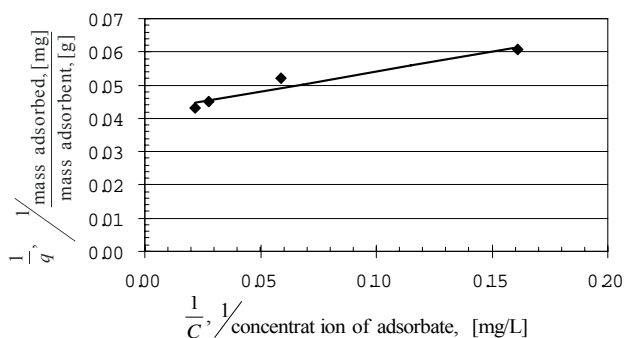


Fig.7 Langmuir isotherm of Se(VI) (conditions: ferric cupric hydroxide 1 g/L; agitation time 2 h; pH 6; T 298 K; initial concentrations of Se 10, 20, 30, 50 mg/L)

The photograph of the surface of adsorbent (i.e. ferric cupric hydroxide) after adsorbing Se(VI) ion is shown in Fig.8. Both Se(VI) and Se(IV) exist on the adsorbent surface. However, X-ray diffraction analysis indicates that the crystal on the adsorbent is $\text{Cu}_4\text{SeO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$. It should be noted that the adsorbed selenium(VI) ions can be eluted and recovered in the concentrated aqueous phase, while the pH of solution is more than 13. Moreover, the cupric ions (Cu^{2+}) can further be dissolved in the solution at low pH

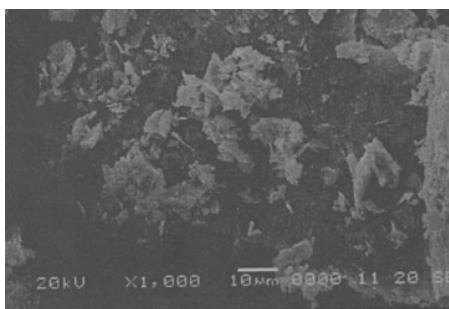


Fig.8 Surface of adsorbent after Se(VI) adsorption

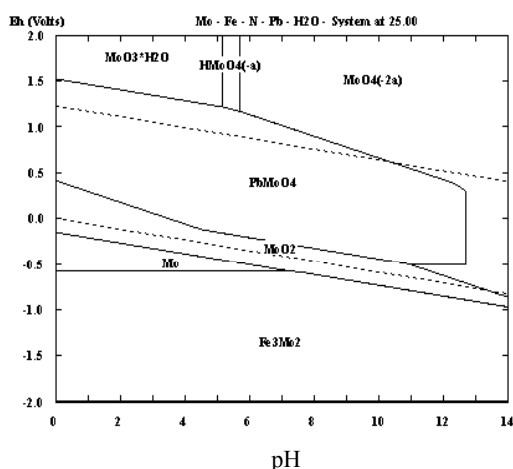


Fig.9 Mo-Fe-Pb-H₂O system at 298 K (conditions: Mo 0.0005 mol/L, Pb, Fe 0.0001 mol/L)

and then adding 5 to 10 g/L zeolite to decrease the concentration of these ions to less than 0.1 mg/L.

3.3 Removal of Molybdenum(VI) Ion

The Eh-pH diagram of the Mo-Pb-Fe-H₂O system is shown in Fig.9. The diagram indicates the thermodynamic stability areas of different species in an aqueous solution containing molybdenum and the prepared adsorbents, i.e. ferric lead hydroxide. The diagram shows the stability areas of different species in the redox potential-pH coordinates. The redox potential axis is based on the standard hydrogen electrode (SHE) scale designated as Eh. It can be seen that the system contains several types of species, such as dissolved ions and solid substances. The lines in the diagram represent the Eh-pH conditions where the content of the adjacent species is in the equilibrium state. Moreover, the upper and lower stability limits of water are shown with dotted lines (Fig.9). The diagram is drawn at constant temperature of 298 K. The molality of each element in the system was 0.5 mmol/L. It can easily be seen that in neutral and caustic conditions PbMoO_4 is very stable. Nevertheless, it can be dissolved as MoO_4^{2-} at pH more than 13 (Fig.9).

The effect of pH on the adsorption rate of Mo(VI) by ferric lead hydroxide is shown in Fig.10. It can be seen that the molybdenum adsorption is carried out well in the acidic region. Moreover, adsorption isotherm of molybdenum(VI) ion on ferric lead hydroxide at pH 9 is shown in Fig.11. It was found that the adsorption capacity increases at the acidic region and reaches its maximum of about 40 mg/g at pH 9. The photograph of the surface of adsorbent (i.e. ferric lead hydroxide), after adsorbing Mo(VI) ion is shown in Fig.12. X-ray diffraction analysis indicated an amorphous structure, however, the measurement of elements and valence by

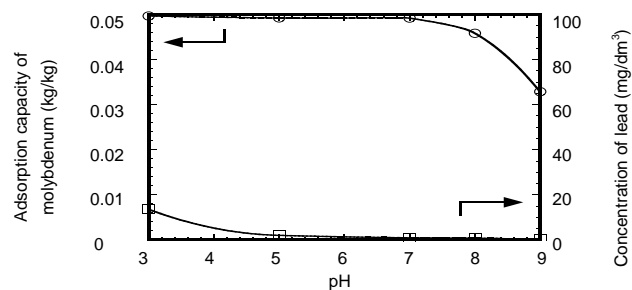


Fig.10 The effect of pH on the adsorption of Mo(VI) ion by the ferric lead hydroxide powder (conditions: $T=298$ K; lead-based adsorbent 1000 mg/L, adsorption period 2 h)

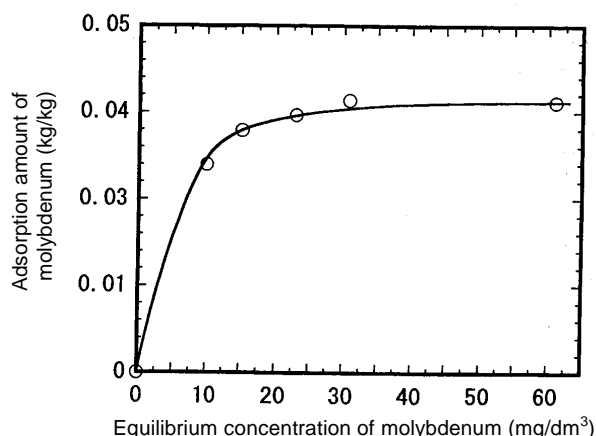


Fig.11 Adsorption isotherm of Mo(VI) ion using ferric lead hydroxide powder (conditions: $T=298\text{ K}$, $\text{pH } 9$)

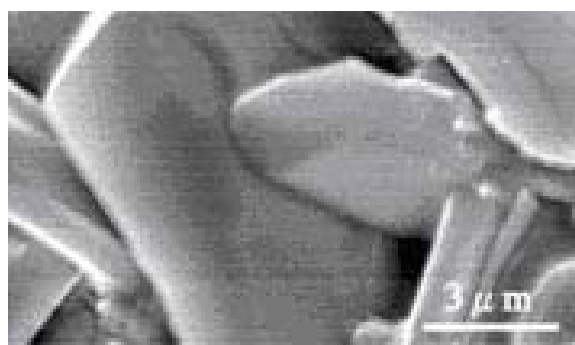


Fig.12 Surface of adsorbent after Mo(VI) adsorption

XPS indicated the formation of thin layer of PbMoO_4 on the surface of the adsorbent. It should be noted that the adsorbed Mo(VI) ion can be eluted at pH more than 13 and recovered in the concentrated aqueous phase. Moreover lead ions (Pb^{2+}) can further be dissolved in the solution at the acidic pH region and then adding 5 to 10 g/L zeolite to decrease the concentration of this ion to less than 0.1 mg/L that is effluent standard level for Pb.

3.4 Removal of Antimony (III) Ion

The Eh–pH diagram of the Sb–Pb–Fe–H₂O system is shown in Fig.13. The diagram indicates the thermodynamic stability areas of different species in an aqueous solution containing antimony and the prepared adsorbents, i.e. ferric lead hydroxide. It can be seen that the system contains several types of species, such as Sb_2O_5 , SbO_2 and Sb_2O_3 .

The effect of pH on the adsorption rate of Sb(III) by ferric lead hydroxide is shown in Fig.14. It can be

seen that the concentration of the sorbed antimony gradually decreases at the alkaline region. Moreover, adsorption isotherm of Sb(III) ion on ferric lead hydroxide at pH 4 is shown in Fig.15. It was found that the adsorption capacity increases at the acidic region and it reached its maximum of about 95 mg/g at pH 4 (Fig.15). The photograph of adsorbent surface (i.e. ferric lead hydroxide) after adsorbing Sb(III) ion is shown in Fig.16. X-ray diffraction analysis indicated an amorphous structure, however, the measurement of elements and valence by XPS indicated the adsorption of Sb(III) or Sb(V) on $\text{Pb}(\text{OH})\text{Cl}$ layer of the adsorbent surface. It should also be noted that there is a possibility of elution of adsorbed Sb(III) ion at the high pH value (Fig.14). Moreover lead ions (Pb^{2+}) can further be dissolved in the solution at the acidic pH region and then adding 5 to 10 g/L zeolite to decrease the concentration of this ion to less than 0.1 mg/L that is effluent standard level for Pb.

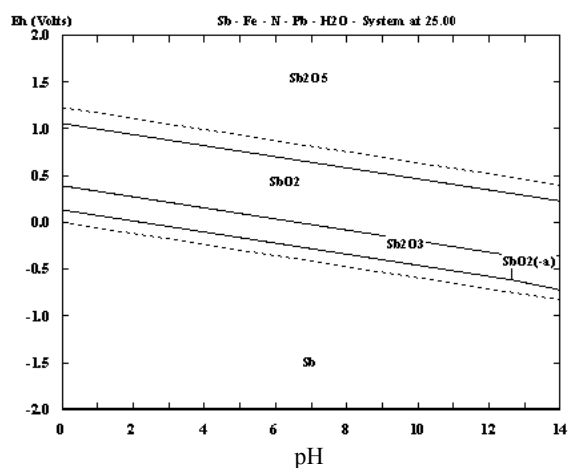


Fig.13 Sb–Fe–Pb–H₂O system at 298 K solution (conditions: Sb 0.0005 mol/L, Pb, Fe 0.0001 mol/L)

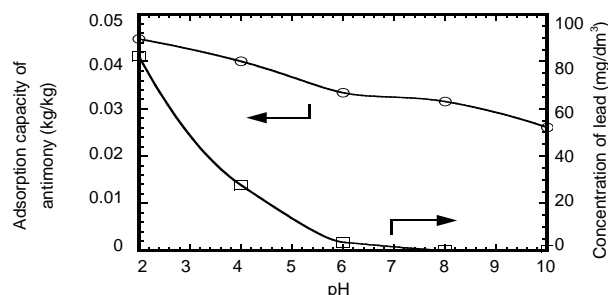


Fig.14 The effect of pH on the adsorption of Sb(III) ion by the ferric lead hydroxide and Pb(II) ion concentration (conditions: $T=298\text{ K}$, lead-based adsorbent 200 mg/L; adsorption period 2 h)

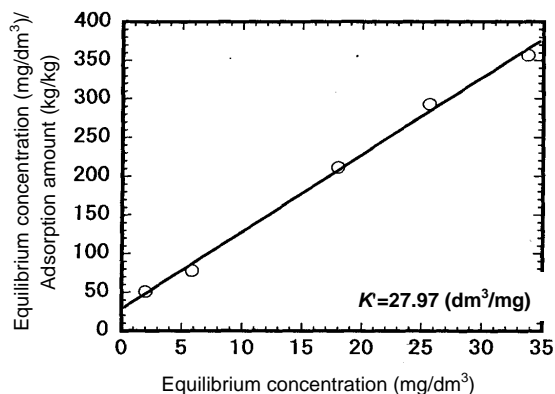


Fig.15 Adsorption isotherm of Sb(III) ion using ferric lead hydroxide powder (conditions: $T=298$ K, pH 4)

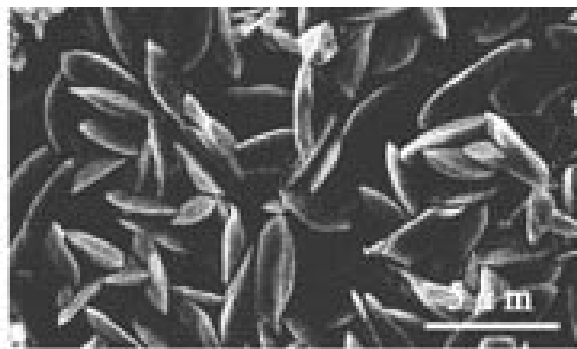


Fig.16 Surface of adsorbent after Sb(III) adsorption

4 CONCLUSIONS

Adsorption behaviors of amorphous hydroxide type adsorbents, i.e. ferric hydroxide, ferric cupric hydroxide and ferric lead hydroxide, were investigated for removing As(III), Se(VI), Mo(VI) and Sb(III) ions from aqueous solutions. The experimental results demonstrated that the adsorption rate of each ion was influenced by both the pH of solution and the concentration of adsorbent.

The newly developed adsorbents have been very effective in removing those ions from artificial wastewater to the concentrations and reducing the contamination levels below the approved ones by the environmental authority in Japan. Finally, it should be noted that the adsorbed ions can be eluted from the surface of adsorbents by controlling pH, creating conditions for recycling of the eluted ions.

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